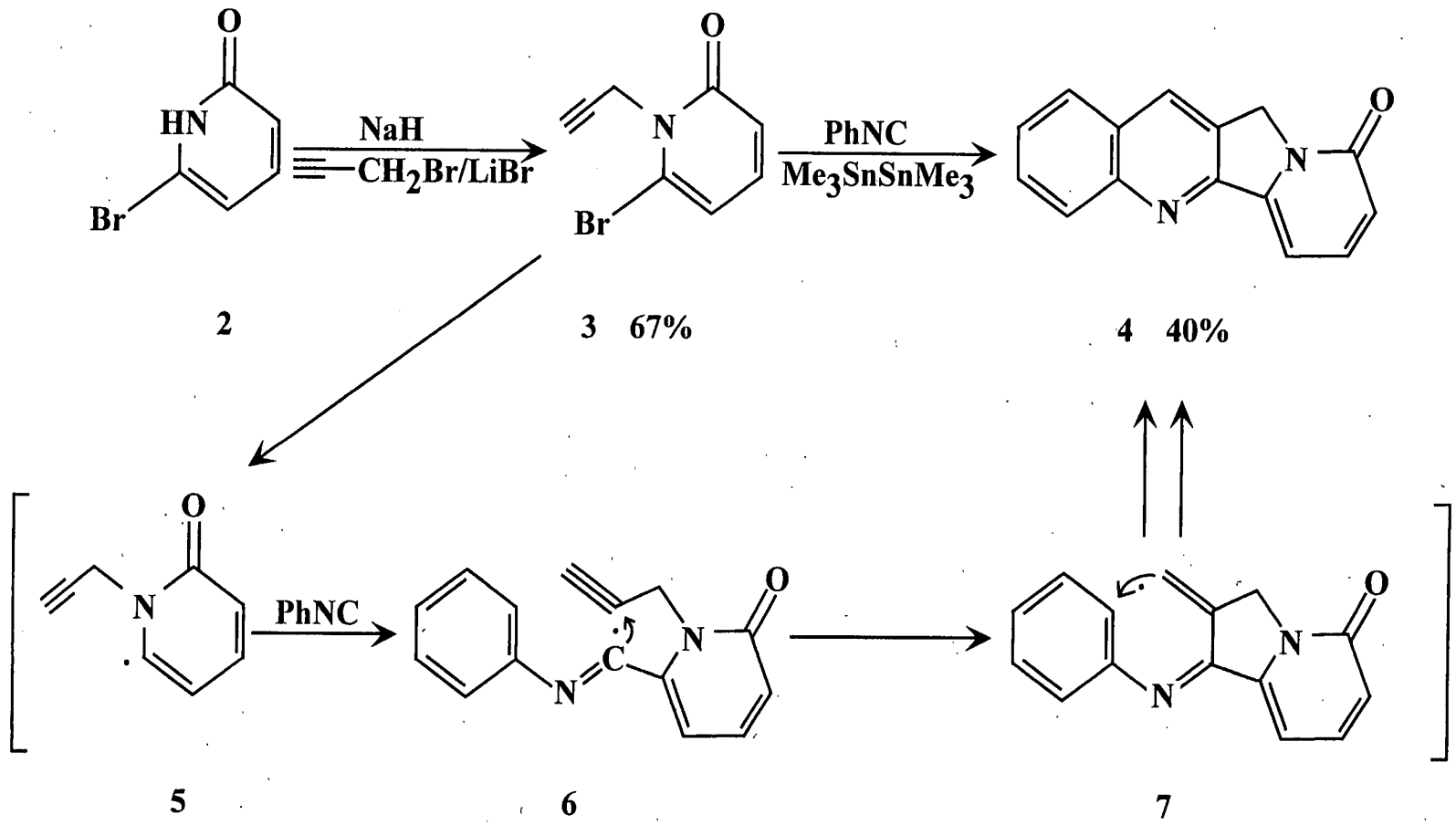

O
HN
Br
NaH
CH2Br/LiBr
N
Br
PhNC
Me3SnSnMe3
N
N
O
2
3 67%
4 40%
O
N
PhNC
N
C
N
O
O
N
N
O
5
6
7

Figure 1

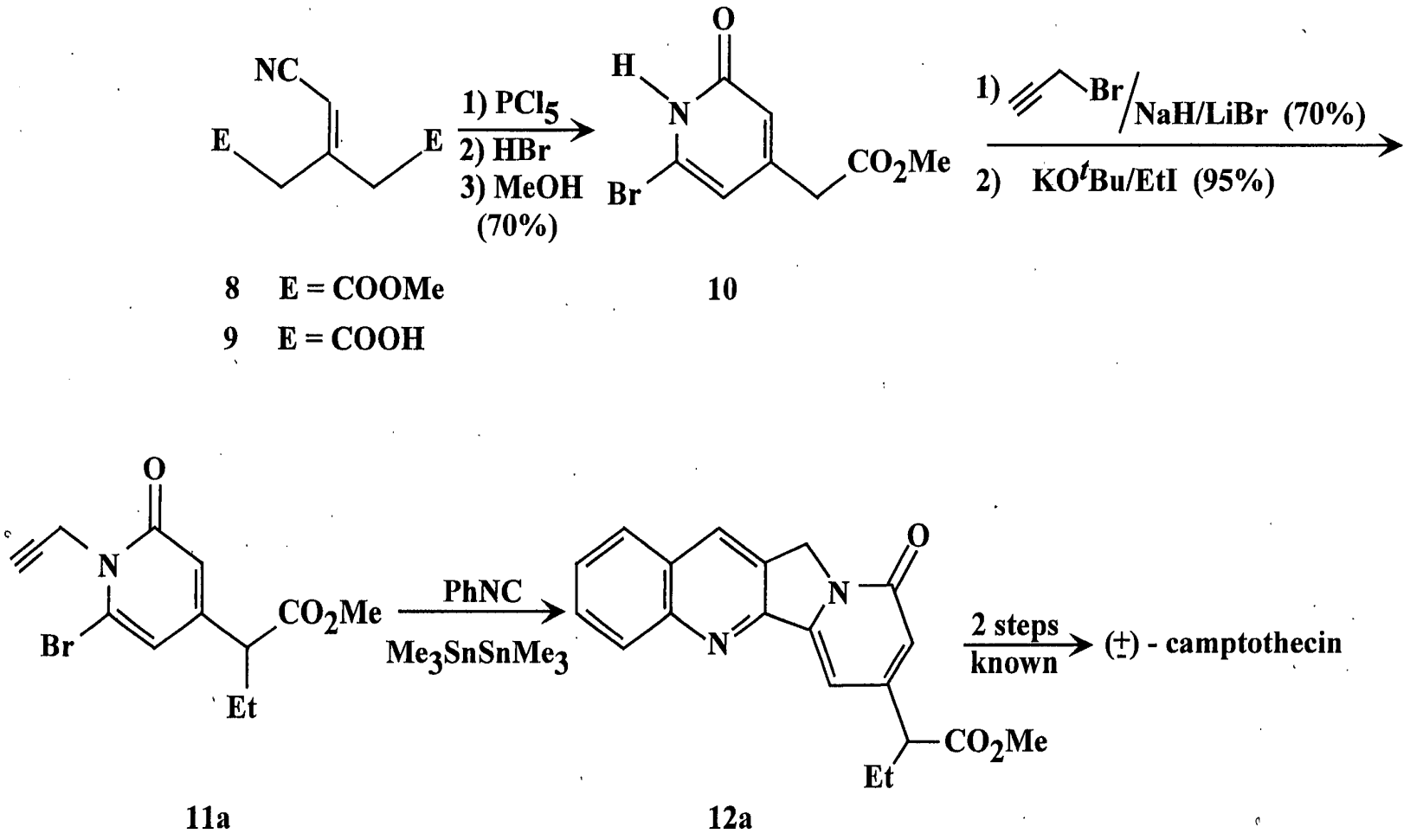

NC
E
E
1) PCl5
2) HBr
3) MeOH
(70%)
O
H
N
Br
CO2Me
1)
Br
NaH/LiBr (70%)
2) KO^tBu/EtI (95%)
8 E = COOMe
9 E = COOH
10
O
N
Br
CO2Me
Et
PhNC
Me3SnSnMe3
O
N
N
2 steps
known
(±) - camptothecin
CO2Me
Et
11a
12a

Figure 2

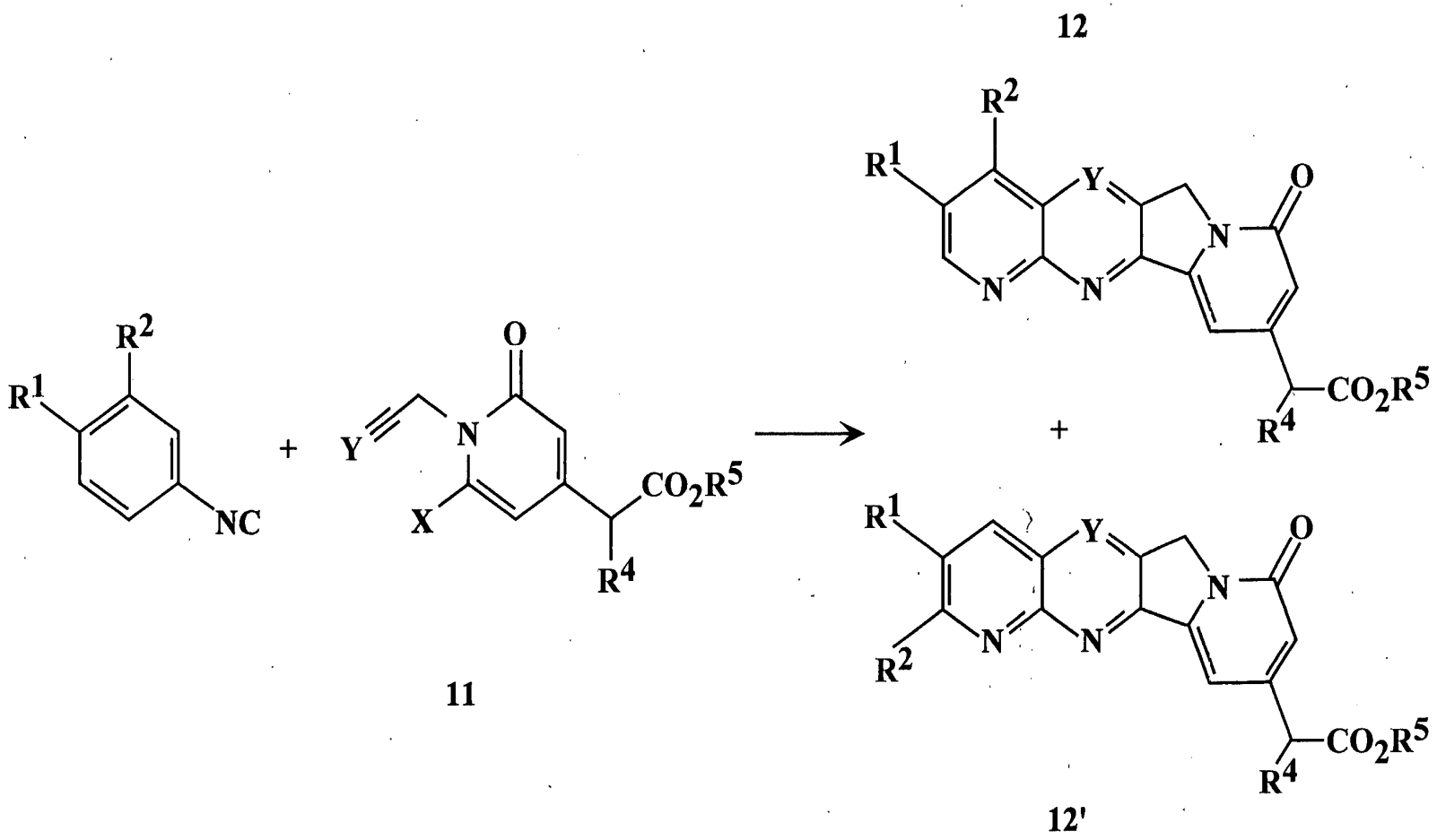
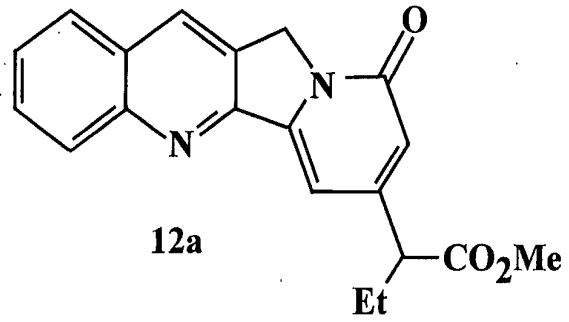
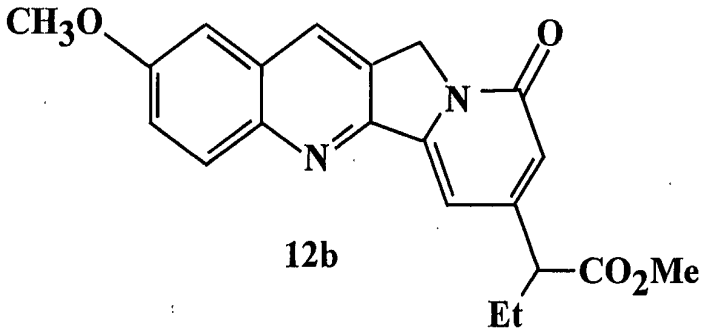

12
R2
R1
Y
O
N
N
N
CO2R5
R4
+
R1
Y
O
N
N
N
R2
CO2R5
R4
12'
R2
R1
NC
+
Y
O
N
X
CO2R5
R4
11

Figure 3



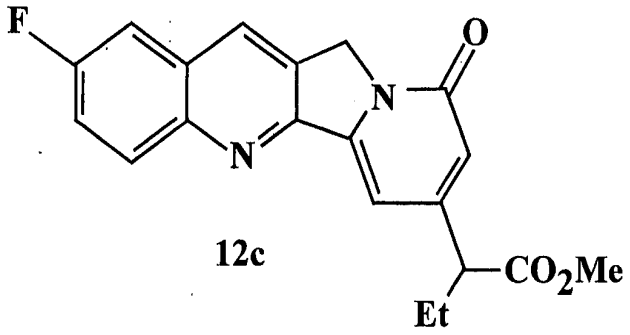
12a

Figure 4a



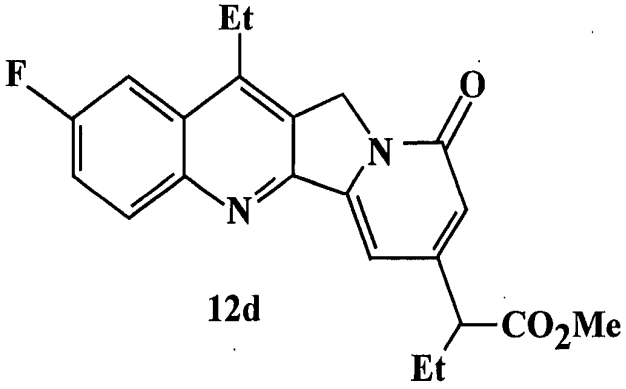
12b

Figure 4b



12c

Figure 4c



12d

Figure 4d

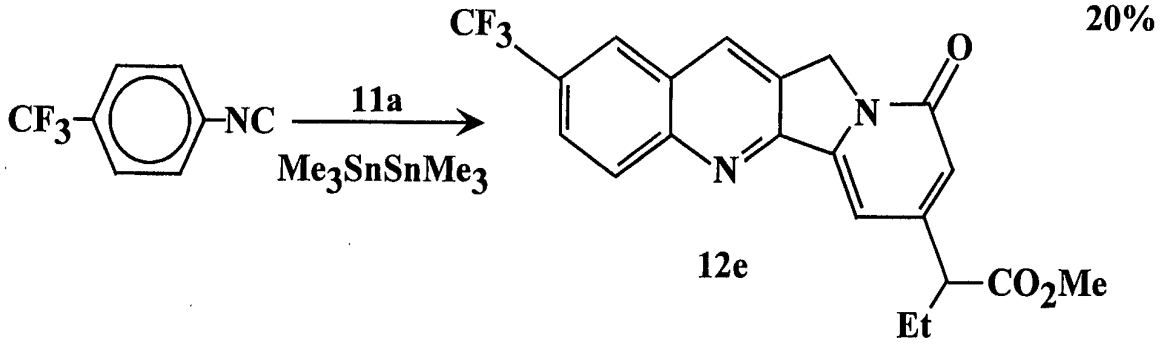


Figure 4e

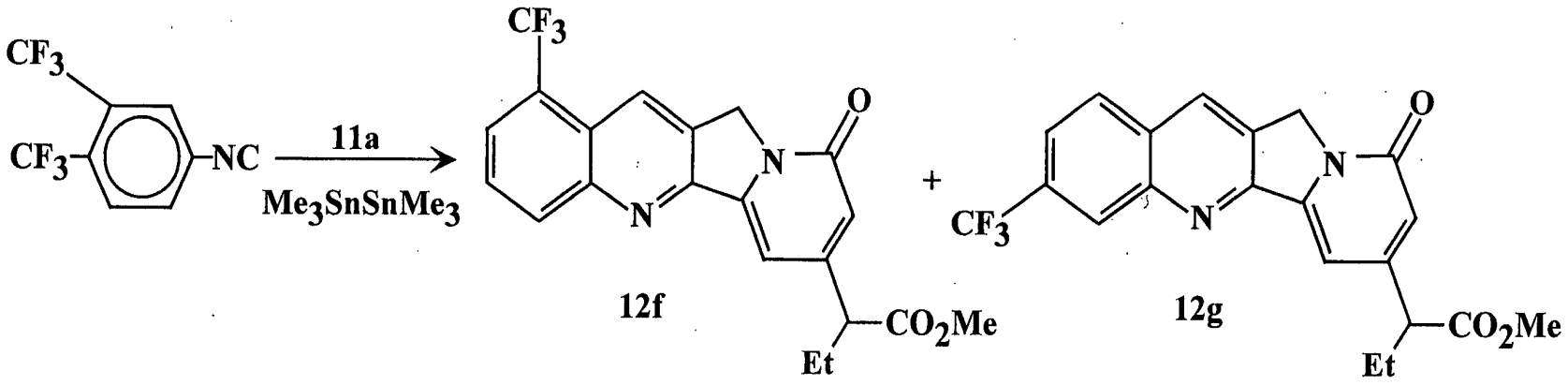


Figure 4f

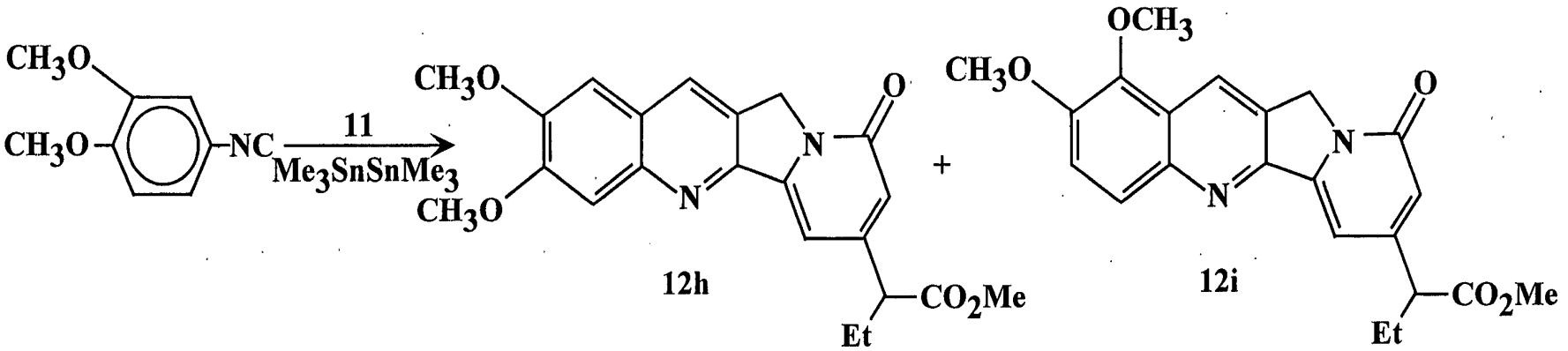

CH3O
CH3O
NC
11
Me3SnSnMe3
CH3O
CH3O
N
O
12h
CO2Me
Et
+
OCH3
CH3O
N
O
12i
CO2Me
Et
4/1, 42%

Figure 4g

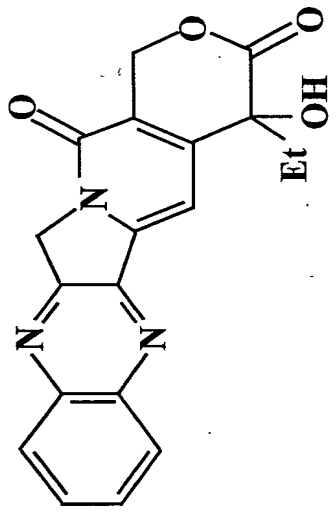
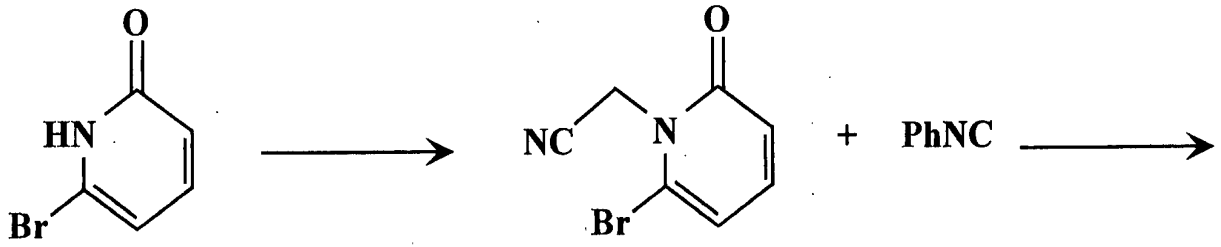
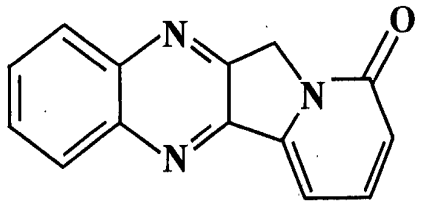


Figure 5

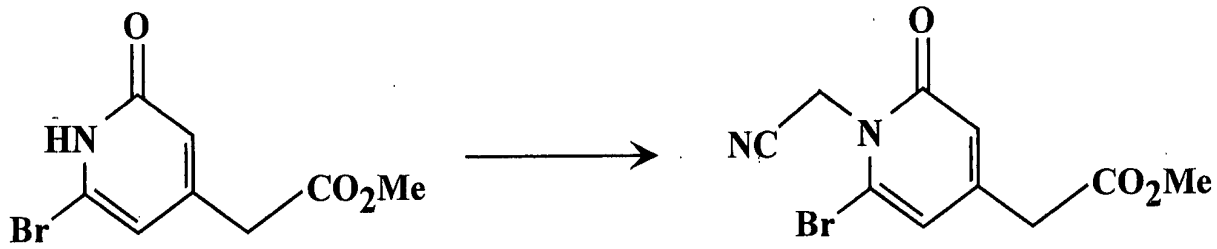


11b



12j

Figure 6



11c

Figure 7

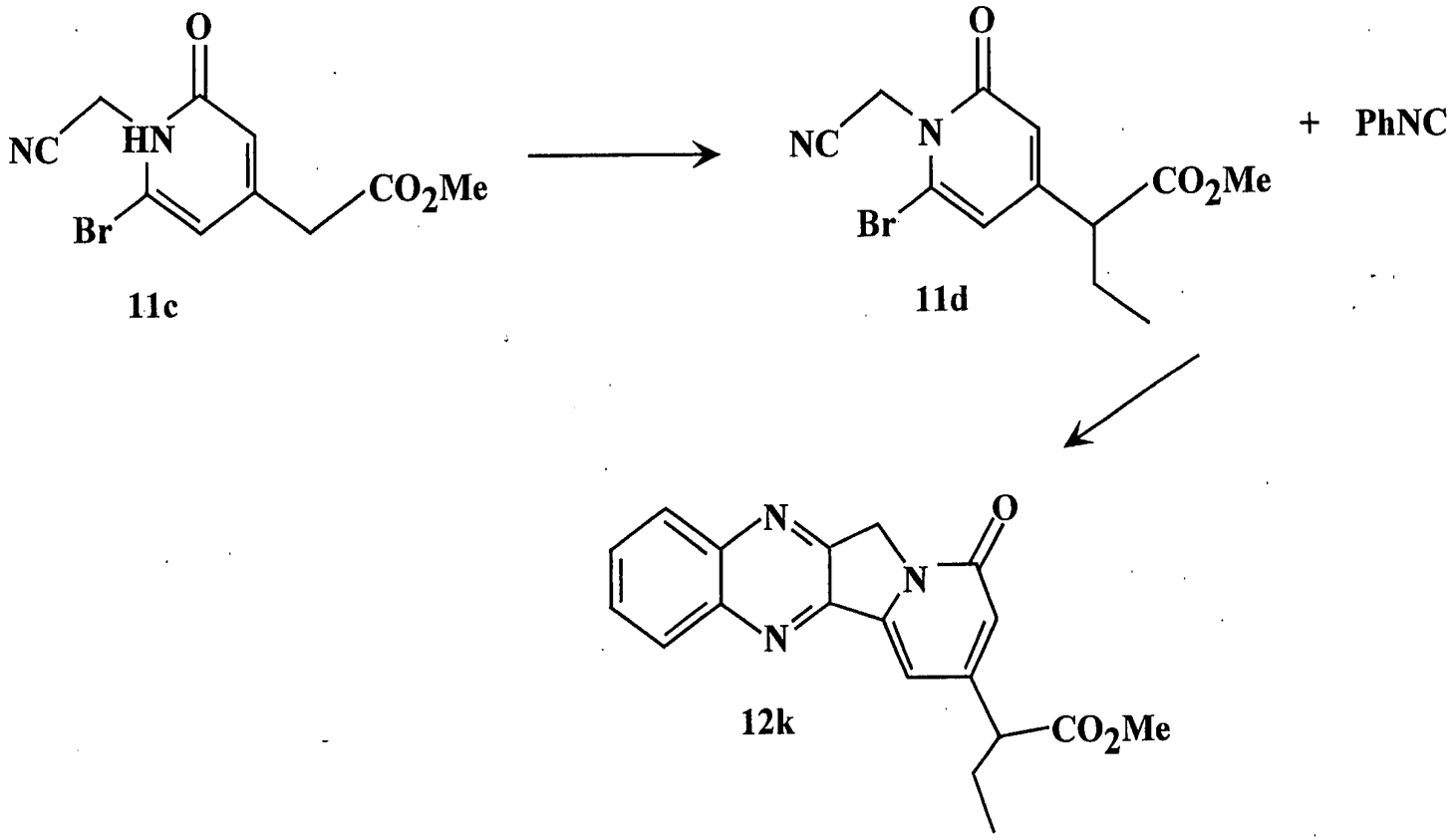


Figure 8

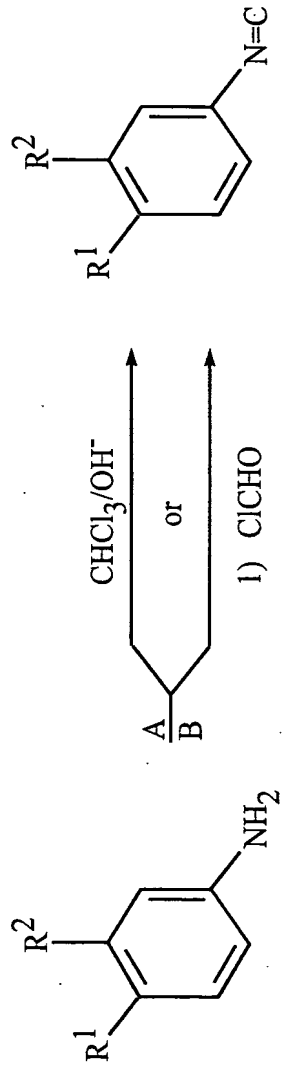


Figure 9

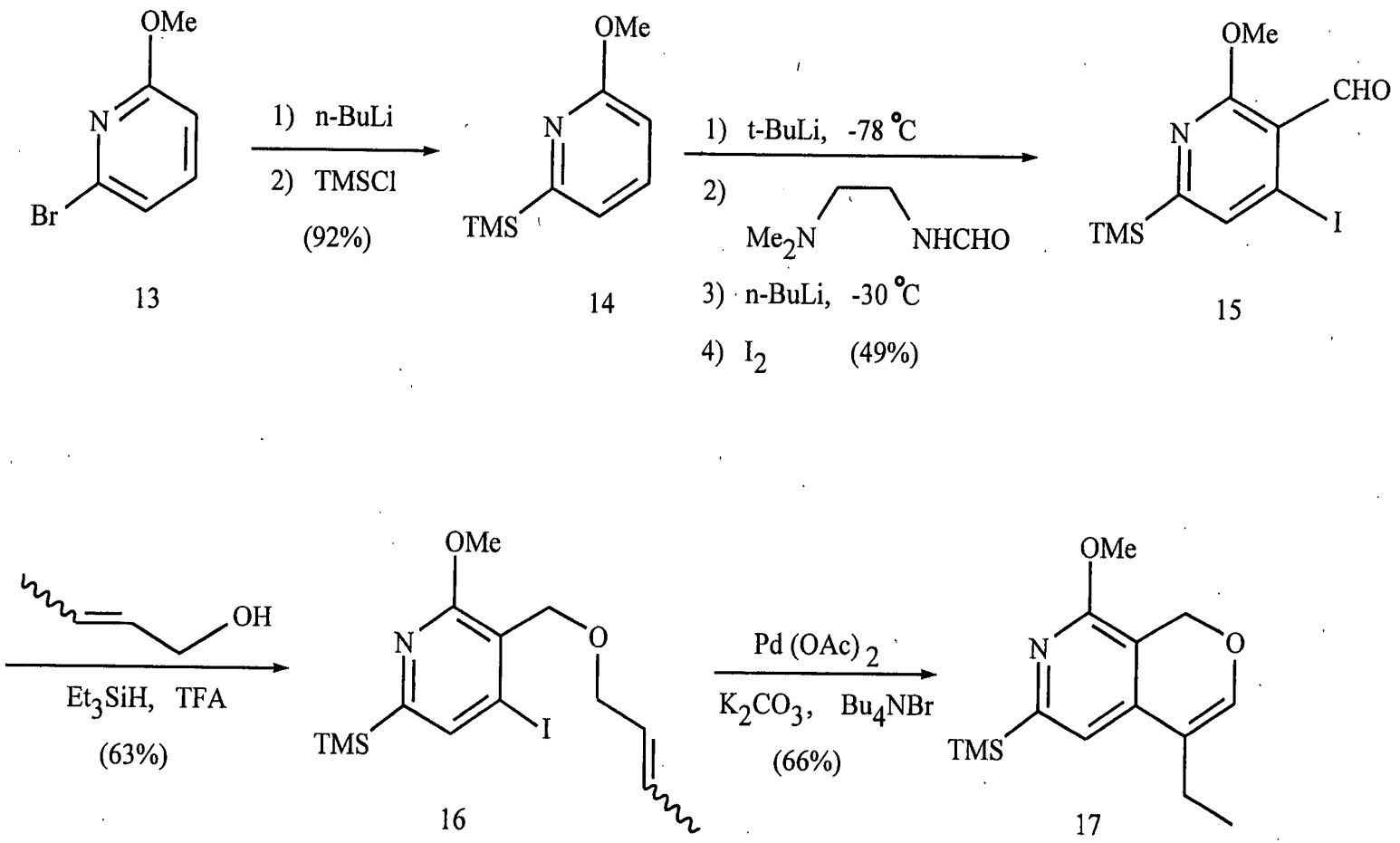

OMe
N
Br
1) n-BuLi
2) TMSCl
(92%)
TMS
13
14
1) t-BuLi, -78 °C
2)
Me2N
NHCHO
3) n-BuLi, -30 °C
4) I2
(49%)
CHO
I
15
OH
Et3SiH, TFA
(63%)
O
16
Pd (OAc) 2
K2CO3, Bu4NBr
(66%)
17

Figure 10A

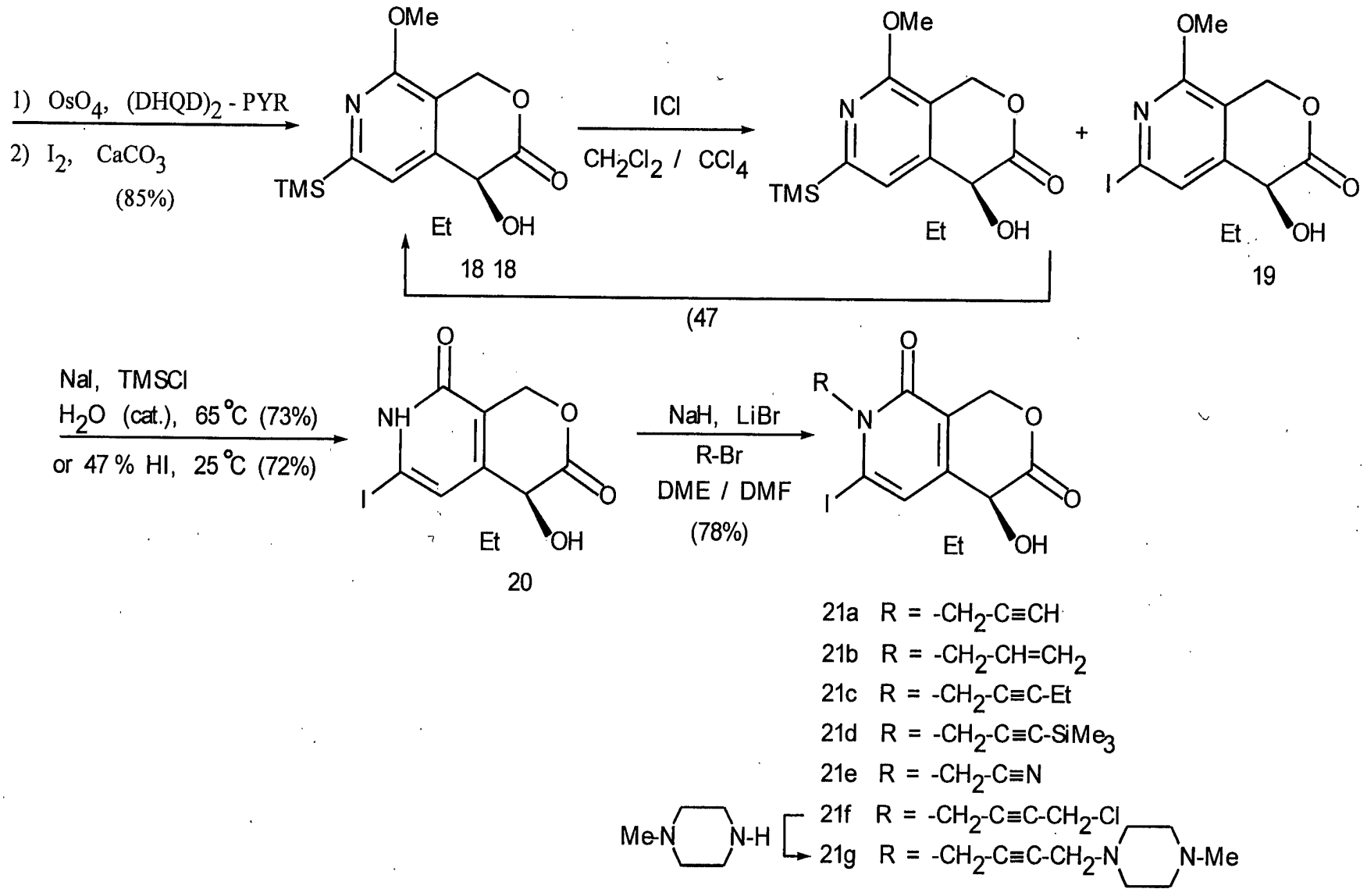
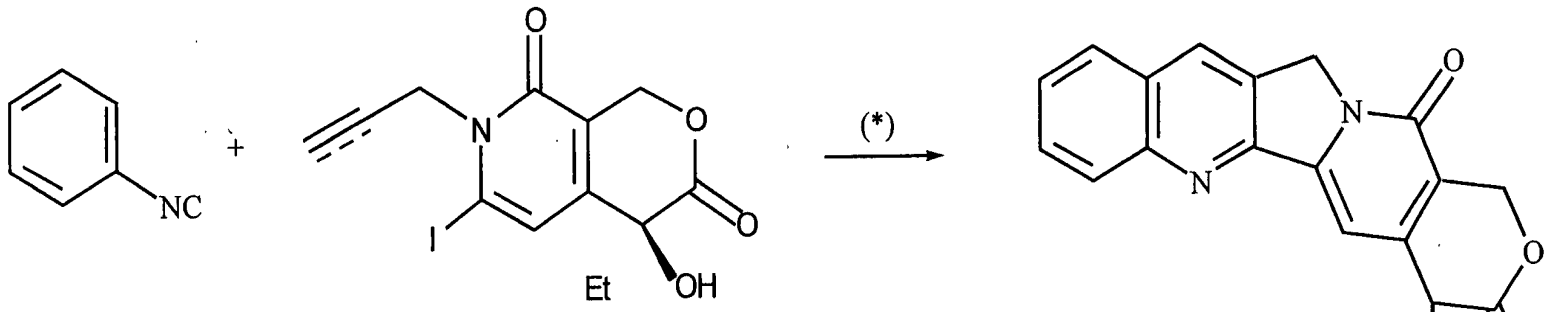

1) OsO_4, $(DHQD)_2$ - PYR
2) I_2, $CaCO_3$
(85%)
ICl
CH_2Cl_2 / CCl_4
OMe
N
O
TMS
Et
OH
18 18
19
(47
NaI, TMSCl
H_2O (cat.), 65 °C (73%)
or 47 % HI, 25 °C (72%)
NH
I
20
NaH, LiBr
R-Br
DME / DMF
(78%)
R
21a R = $-CH_2-C\equiv CH$
21b R = $-CH_2-CH=CH_2$
21c R = $-CH_2-C\equiv C-Et$
21d R = $-CH_2-C\equiv C-SiMe_3$
21e R = $-CH_2-C\equiv N$
21f R = $-CH_2-C\equiv C-CH_2-Cl$
21g R = $-CH_2-C\equiv C-CH_2-N$
Me-N
N-H
N-Me

Figure 10B



21a, alkyne

21b, alkyne

1a

(*) : 21a, $Me_3SnSnMe_3$, benzene, 70°C, 5 h — 63 %

21a, $Me_3SiSiMe_3$, benzene, 70°C, 8 h — 52 %

21a, $Me_3SnSnMe_3$, t-BuOH, 70°C, 6 h — 45 %

21b, $Me_3SnSnMe_3$, benzene, 70°C, 8 h — 21 %

Figure 11

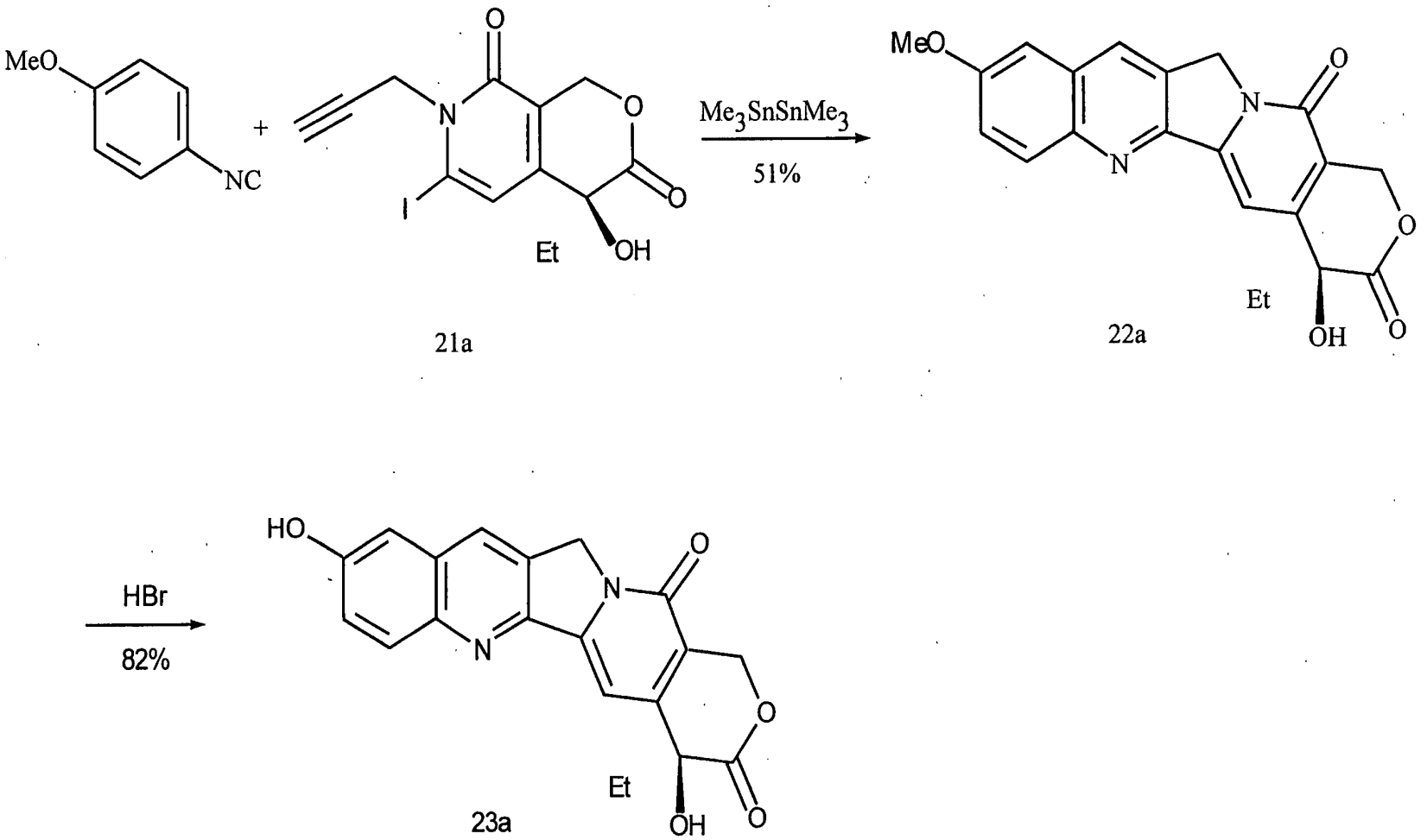

MeO
NC
+
O
N
O
O
I
Et
OH
21a
$Me_3SnSnMe_3$
51%
MeO
N
N
O
O
O
Et
OH
O
22a
HBr
82%
HO
N
N
O
O
O
Et
OH
O
23a

Figure 12

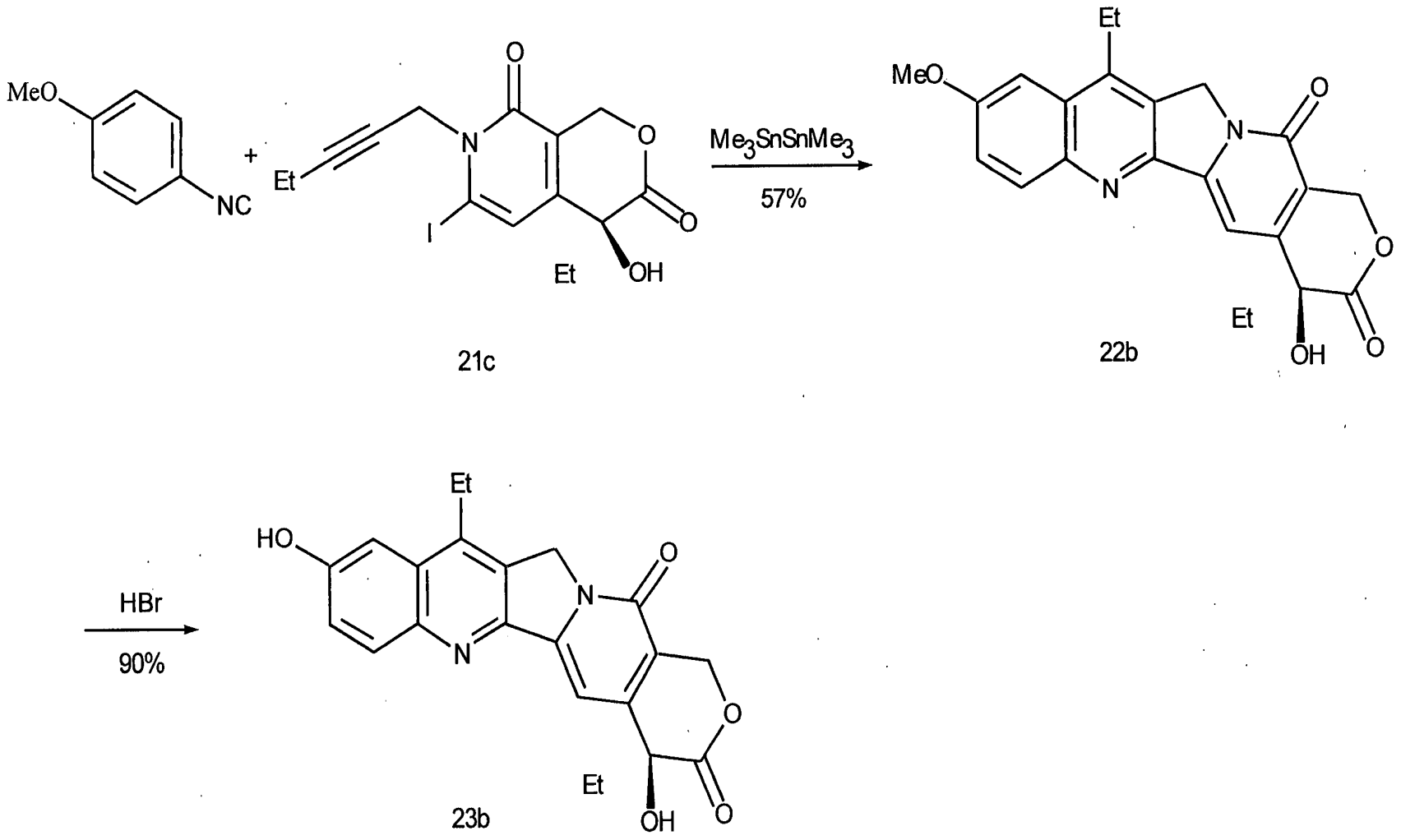

MeO
NC
+
Et
I
O
N
O
O
Et
OH
21c
Me3SnSnMe3
57%
MeO
Et
N
N
O
O
Et
OH
O
22b
HBr
90%
HO
Et
N
N
O
O
Et
OH
O
23b

Figure 13

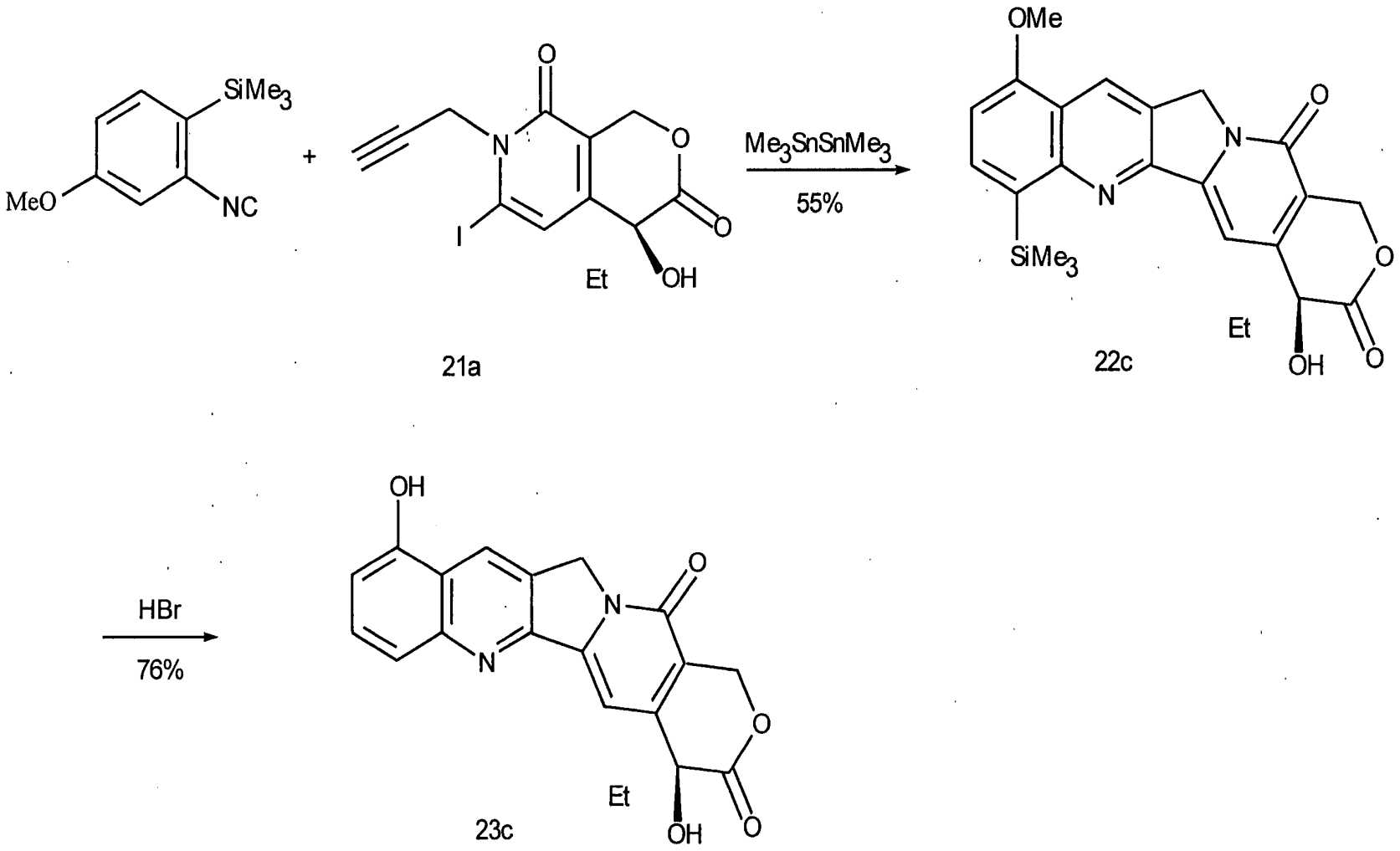

SiMe3
MeO
NC
+
O
N
O
O
I
Et
OH
21a
Me3SnSnMe3
55%
OMe
N
O
N
SiMe3
O
Et
OH
O
22c
HBr
76%
OH
N
O
N
O
Et
OH
O
23c

Figure 14

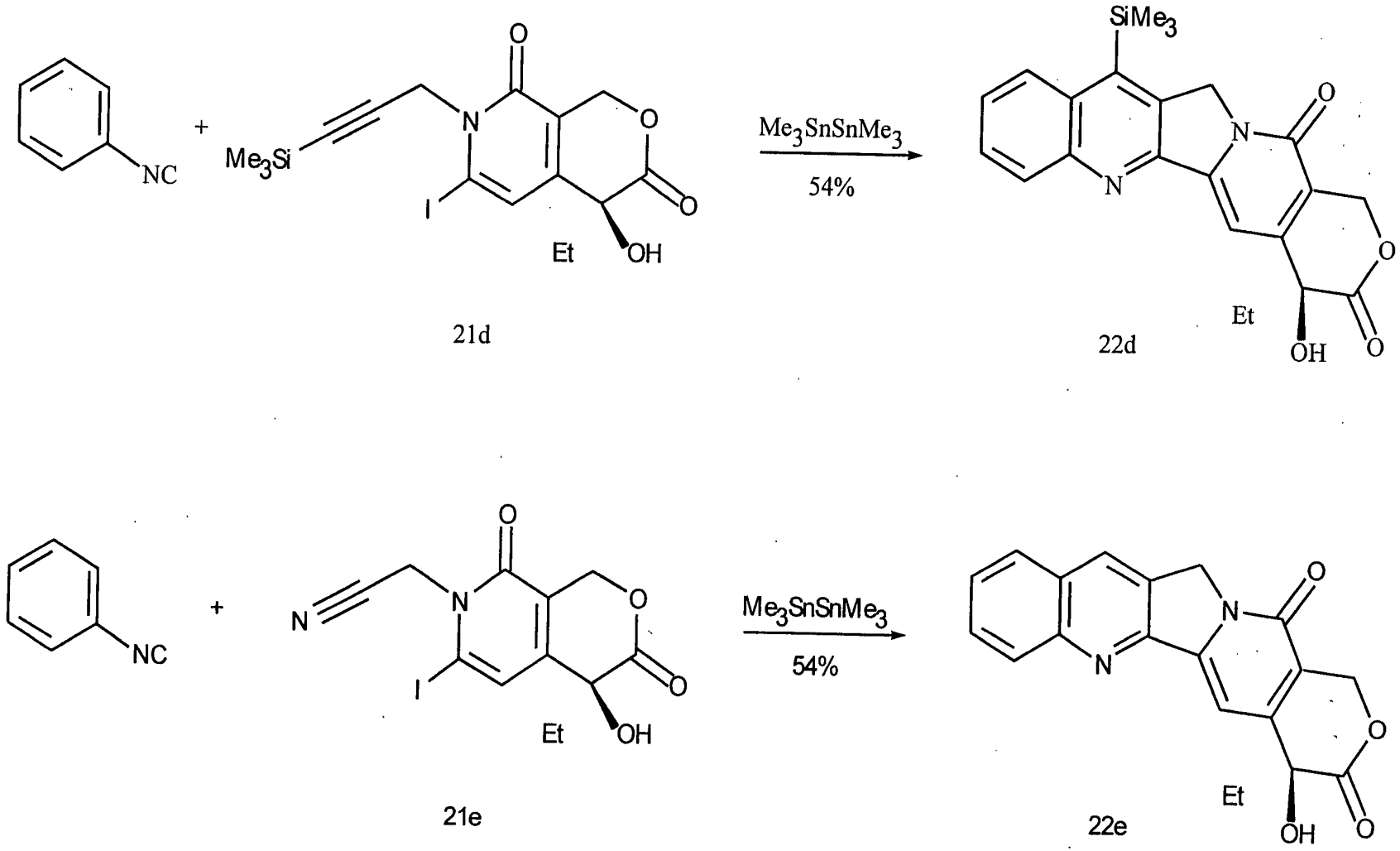

NC
Me3Si
I
Et
OH
21d
Me3SnSnMe3
54%
SiMe3
22d
NC
N
I
Et
OH
21e
Me3SnSnMe3
54%
22e

Figure 15

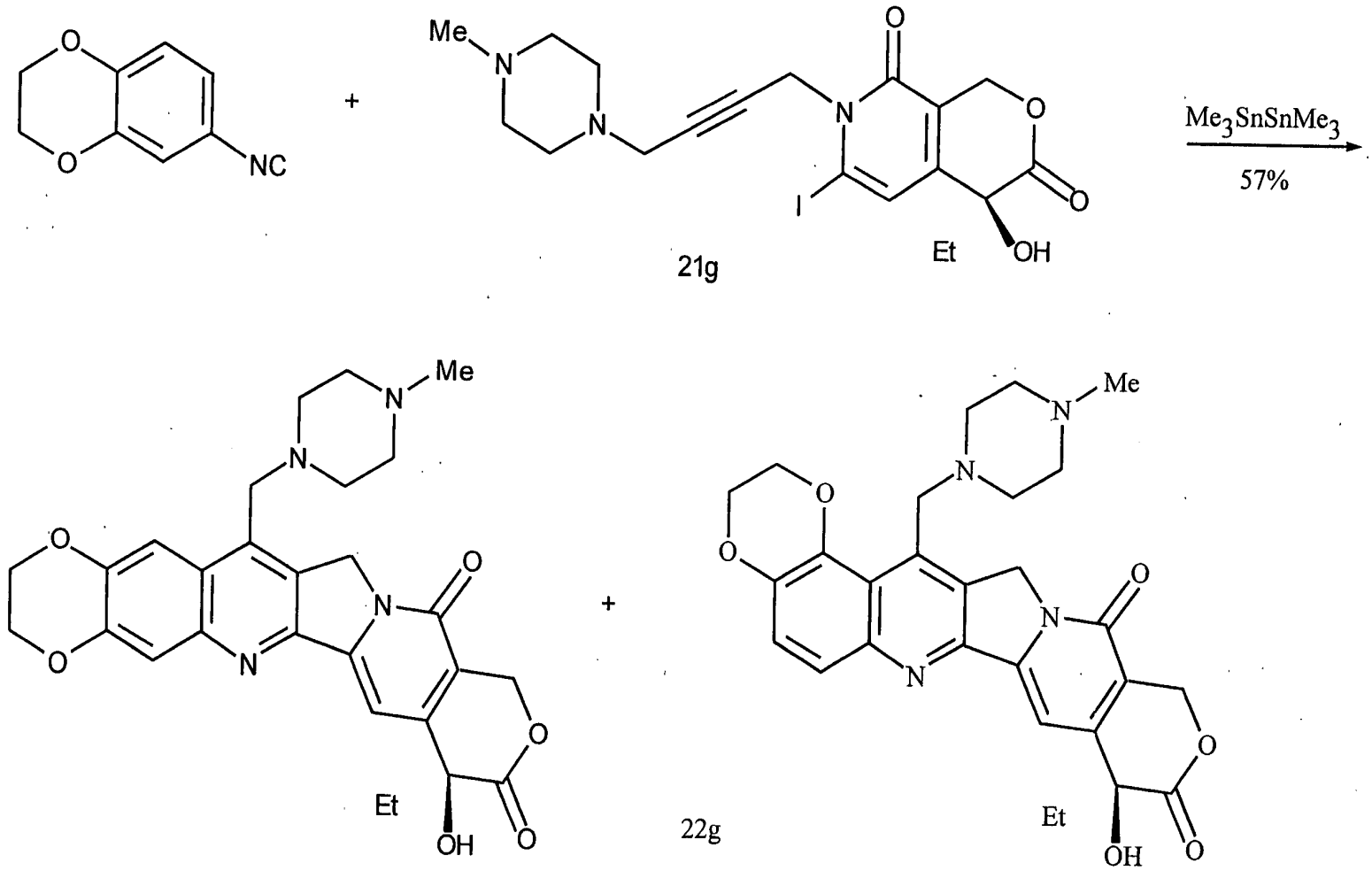

Me
N
N
O
O
O
O
O
I
Et
OH
21g
$Me_3SnSnMe_3$
57%
NC
+
Me
N
N
O
O
O
O
N
O
Et
OH
O
+
22g
Me
N
N
O
O
O
O
N
O
Et
OH
O

Figure 16